UNIVERSITI PUTRA MALAYSIA

INTERACTION OF POLY(ETHYLENEGLYCOL) ETHER IN ISOTROPIC REGION, L2, OF MIXED SODIUM DODECYL SULPHATE (SDS) - SODIUM CAPRYLATE (SCA) SYSTEM

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By

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SDS	Sodium Dodecyl Sulphate
SCA	Sodium Caprylic Acid
PEG8,000	Poly(ethylene glycol) ether
mPEG2,000	Poly(ethylene glycol) monomethoxy ether
$C_6H_{13}OH$	1-hexanol
$C_{10}H_{22}$	n-decane
w/o	water in oil
o/w	oil in water

Abstract of thesis submitted to the Senate of Universiti Pertanian Malaysia in fulfilment of the requirement for the degree of Master of Science.

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August 1996

Chairman : Assoc. Prof. Dr. Hamdan Suhaimi

Faculty : Science and Environmental Studies

Mixed surfactants of SDS-SCA at weight ratio of 2:3 in SDS-SCA/ $C_6H_{13}OH/H_2O$ system gives the largest inverse micelle region. This system is used for further construction of the w/o microemulsion phase diagram where n-decane is added into the system. The SDS-SCA-$C_6H_{13}OH/C_{10}H_{22}/H_2O$ system shows a larger w/o microemulsion region than the pure surfactants in surfactant/1-hexanol/n-decane/water system. Maximum water solubility is found at 65.0 weight percent of n-decane and 35.0 weight percent of SDS-SCA-$C_6H_{13}OH$. Polymers, mPEG2,000 and PEG8,000 are then added into the line above in the solution. The SDS-SCA-$C_6H_{13}OH$-$C_{10}H_{22}/H_2O$/mPEG2,000 system is observed to have a bigger isotropic region than the SDS-SCA-$C_6H_{13}OH$-$C_{10}H_{22}/H_2O$/PEG8,000 system. These two

systems are sensitive to temperature where the isotropic region change dramatically as temperature is increased.

Nuclear Magnetic Resonance (NMR) is used to detect the interaction and the degree of freedom of the molecules in the isotropic solution which consist of SDS, SCA, $C_6H_{13}OH$, $C_{10}H_{22}$ and H_2O. This instrument is able to detect the formation of the inverse micelle and the w/o microemulsion in the SDS-SCA/$C_6H_{13}OH$/H_2O and SDS-SCA-$C_6H_{13}OH$/$C_{10}H_{22}$/H_2O systems. The only interaction between the molecules are found in the SDS-SCA-$C_6H_{13}OH$-$C_{10}H_{22}$/H_2O/mPEG2,000 and the SDS-SCA-$C_6H_{13}OH$-$C_{10}H_{22}$/H_2O/PEG8,000 systems.

The viscosity of the solution confirms that the inverse micelle and the w/o microemulsion are formed in the SDS-SCA/$C_6H_{13}OH$/H_2O and SDS-SCA-$C_6H_{13}OH$/$C_{10}H_{22}$/H_2O systems. It is observed that the aggregations are not geometrically packed together. The presence of the polymers, mPEG2,000 and PEG8,000 in the SDS-SCA-$C_6H_{13}OH$/$C_{10}H_{22}$/H_2O system can break the w/o microemulsion.

Abstrak tesis yang dikemukakan kepada Senat Universiti Pertanian Malaysia sebagai memenuhi syarat untuk Ijazah Master Sains

KAJIAN TERHADAP INTERAKSI POLI(ETILENE GLIKOL) ETER DI KAWASAN ISOTROPIK, L_2, YANG MENGANDUNGI CAMPURAN NATRIUM DODESIL SULFAT (SDS) - NATRIUM KAPRILAT (SCA)

Oleh

LIM WEN HUEI

Ogos 1996

Pengerusi : Prof. Madya Dr. Hamdan Suhaimi

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Campuran surfaktan SDS dan SCA pada nisbah berat 2:3 dalam sistem SDS-SCA/$C_6H_{13}OH/H_2O$ menghasilkan satu kawasan misel songsang yang luas. Nisbah berat 2:3 ini digunakan untuk kajian selanjutnya dalam penghasilan w/o mikroemulsi dengan menambah n-dekana yang bertindak sebagai minyak. Sistem SDS-SCA-$C_6H_{13}OH/C_{10}H_{22}/H_2O$ mempunyai kawasan w/o microemulsi yang luas jika dibandingkan dengan sistem SDS-$C_6H_{13}OH/C_{10}H_{22}/H_2O$ dan sistem SCA-$C_6H_{13}OH/C_{10}H_{22}/H_2O$. Kelarutan air yang maksimum didapati pada garis 65 berat peratus n-dekana and 35 berat peratus SDS-SCA-$C_6H_{13}OH$. Polimer iaitu mPEG2,000 dan PEG8,000 akan ditambahkan pada garis di atas. Kedua-dua sistem ini, iaitu SDS-SCA-$C_6H_{13}OH$-$C_{10}H_{22}/H_2O$/mPEG2,000 and SDS-SCA-$C_6H_{13}OH$-$C_{10}H_{22}$ /H_2O/PEG8,000 sensitif terhadap suhu di mana kawasan isotropik berubah

dengan kenaikan suhu. Kawasan satu fasa bagi sistem SDS-SCA-$C_6H_{13}OH$-C_{10}

$C_{10}H_{22}$ /H_2O/PEG8,000.

NMR digunakan untuk mengesan interaksi dan darjah kebebasan molekul dalam larutan ini yang mengandungi SDS, SCA, $C_6H_{13}OH$, $C_{10}H_{22}$ dan H_2O. Ia dapat mengesan pembentukan misel songsang dan microemulsi air dalam minyak dalam sistem SDS-SCA/$C_6H_{13}OH$/H_2O and sistem SDS-SCA-$C_6H_{13}OH$/$C_{10}H_{22}$ /H_2O. Sistem SDS-SCA-$C_6H_{13}OH$-$C_{10}H_{22}$/H_2O/mPEG2,000 dan sistem SDS-SCA-$C_6H_{13}OH$-$C_{10}H_{22}$ /H_2O/PEG8,000 hanya menunjukkan interaksi berlaku (tiada pembentukan misel songsang dikesan).

Kelikatan larutan menunjukkan bahawa misel songsang dan microemulsi air dalam minyak terbentuk dalam sistem SDS-SCA/$C_6H_{13}OH$/H_2O and sistem SDS-SCA-$C_6H_{13}OH$/ $C_{10}H_{22}$ /H_2O. Aggregasi ini tidak disusun secara geometri dalam larutan tersebut. Kehadiran polimer iaitu mPEG2,000 dan PEG8,000 dalam sistem SDS-SCA-$C_6H_{13}OH$/$C_{10}H_{22}$/H_2O didapati memecahkan microemulsi air dalam minyak dalam larutan.

CHAPTER I

INTRODUCTION

If two immiscible liquids (usually water and oil) are shaken together, they will naturally separate spontaneously into two distinct layers. Suppose instead of merely shaking the two liquids together, a surfactant which often called an emulsifying agent is added into it (Tadros, 1984; Rosen, 1978). The compounds are vigorously mix in a homogeniser, then the milling together of the constituents causes one to be dispersed (the inner phase) in the other (the continuous phase), where an emulsion is produced (Becher, 1983; Vold and Vold, 1983; Shinoda and Friberg, 1986; Florence and Whitehill, 1982). This macroemulsion may be kinetically stable for a long period of time, but in the end, it will suffer the same fate as above, which is phase separation, in order to attain a minimum interfacial free energy (although effort can be made to decrease kinetic rate constants but the thermodynamic drive force remains unchanged, that is to minimise the interfacial area of contact between immiscible phase). A transparent or slightly bluish solution (because these particles are much smaller than the wavelength of visible light) is formed when a suitable composition of the system (contains surfactant, co-surfactant or oil and water) is reached.

This so-called microemulsion is formed when the chemical systems containing oil, water or an aqueous salt solution, surfactant and sometimes a co-surfactant such as alcohol (of an intermediate chain length) are mixed together (Prince, 1977; Mittal, 1976; Elworthy *et al.*, 1968; Schulman *et al.*, 1959; Bourrel and Szhechter, 1988). It appear to be thermodynamically stable compositions and it has an essentially infinite lifetime, assuming that there are no changes in such factors as composition, temperature, and pressure (Overbeek, 1978; Adamson, 1969; Van Vourst Vader, 1960).

The question is, does this transparent solution contain microemulsions or micelles? Micelles do exist in clear solutions too (Elworthy *et al.*, 1968; Rosen, 1978; Mittal, 1979). When one compares microemulsions and micelles, the demarcation line can become quite blurred and, in some it does not even exist. Clearly there is some disagreement as to the true definition of clear isotropic solution as microemulsions [where some prefer the names "swollen micelles solutions" or "solubilised micellar solutions"] or micelles (Winsor, 1948). Some distinguish these microemulsions and micelles solutions by the degree of arbitraries, especially in view of the continuity, that one observes in the physical properties such as the increased of solubility. One possible definition is to assert that a microemulsion is composed of bulk isotropic oil and water regions separated by an anisotropic layer. The interior of a micelle, the oil region, is composed entirely of the lipophilic portions of the amphiphile and is probably not isotropic. But even a micelle containing a small quantity of solubilisate has an isotropic interior. However, as the amounts of oil and water in the micellar solution both become large and approximately of the same volume, it would be

anticipated that bulk isotropic oil and water regions would essentially at some point both exist. However, a microemulsion is thought to be distinct and separate from a micellar solution even though there is no existing technique to distinguish between these two states of matter.

Figure 1 shows the difference between inverse micelle, w/o microemulsion and w/o emulsion. The term microemulsion was coined in 1958 by Schulman and workers to describe a fairly specific class of colloidal system (Schulman *et al.*, 1959). Various experimental approaches have been used in an attempt to ascertain all of the details of their thermodynamic and structural characteristics (Prince, 1977; Mittal, 1976; Bourrel and Szhechter, 1988). It was found that this transparent or translucent system formed spontaneously when oil and water were mixed with relatively large amounts of combined surfactant with co-surfactant. As a result, new theories of the formation and stability of these complex systems were developed, depend on their preparation and the relationships among the chemical structure of the oil phase, the compositions of the aqueous phase, and the structure of the surfactant and co-surfactant (Bourrel and Szhechter, 1988).

A microemulsion normally has droplet diameters of 100 nm or less (up to 5 nm). It is slightly larger than micellar systems because microemulsion is much smaller than the wavelength of visible light. The formation of a microemulsion must have a very specific compositions and chemical structures of various components, that the nomenclature for this separate class of dispersed species has developed. Many

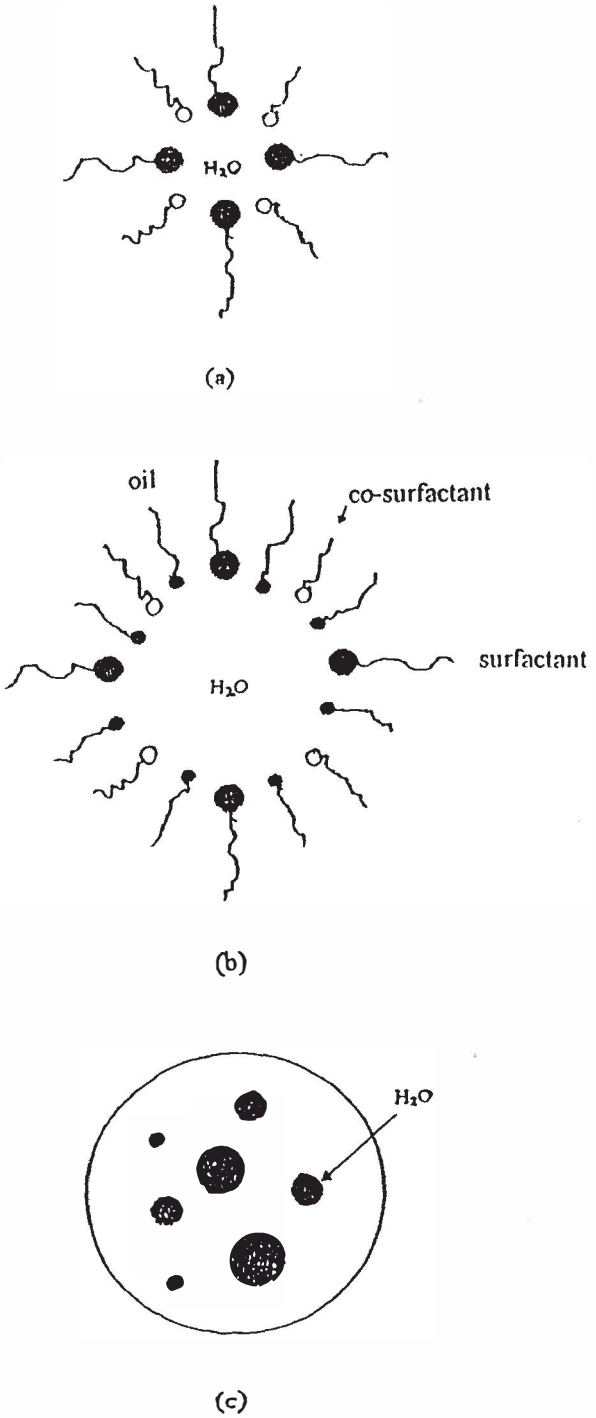

Figure 1: Structures of (a) Inverse micelle (b) w/o microemulsion and (c) w/o emulsion.

microemulsion systems have been described in which the dispersed phase to surfactant (and co-surfactant) ratio exceeds 100, and the high additive to surfactant ratio requires that there be a core of dispersed material that is essential to the bulk phase of the additive (Tadros, 1984). Therefore continuous transitions occur from molecular solution via swollen micelles (or inverse micelle) to microemulsion where the transition from swollen micelles to microemulsions can only be located arbitrarily at a radius of the order of 3 nm.

If one constructs a spectrum of the possible situations for the dispersion of one liquid phase in another, oil in water (o/w), for instance, the possible sizes of the dispersed phase units range from the molecular dispersed solution where "droplet" sizes are on the order of a few nanometers to macroemulsion with droplets of hundreds or thousands of nanometers, as shown in Figure 2. These classifications as shown are certainly arbitrary in their ranges and some overlap inevitably occurs.

Mixed Surfactants

All in all, the formation of micelle or inverse micelle to w/o (water in oil) or o/w (oil in water) microemulsion and emulsion (whether w/o or w/o) is due to the presence of an active compound namely surfactant (Ottewil, 1983). A surfactant or surface active agent, is a substance that when present at low concentration in a system has the property of absorbing onto the surfaces or the interfaces of the system, and thus altering to a marked degree of the surface (or interface) free

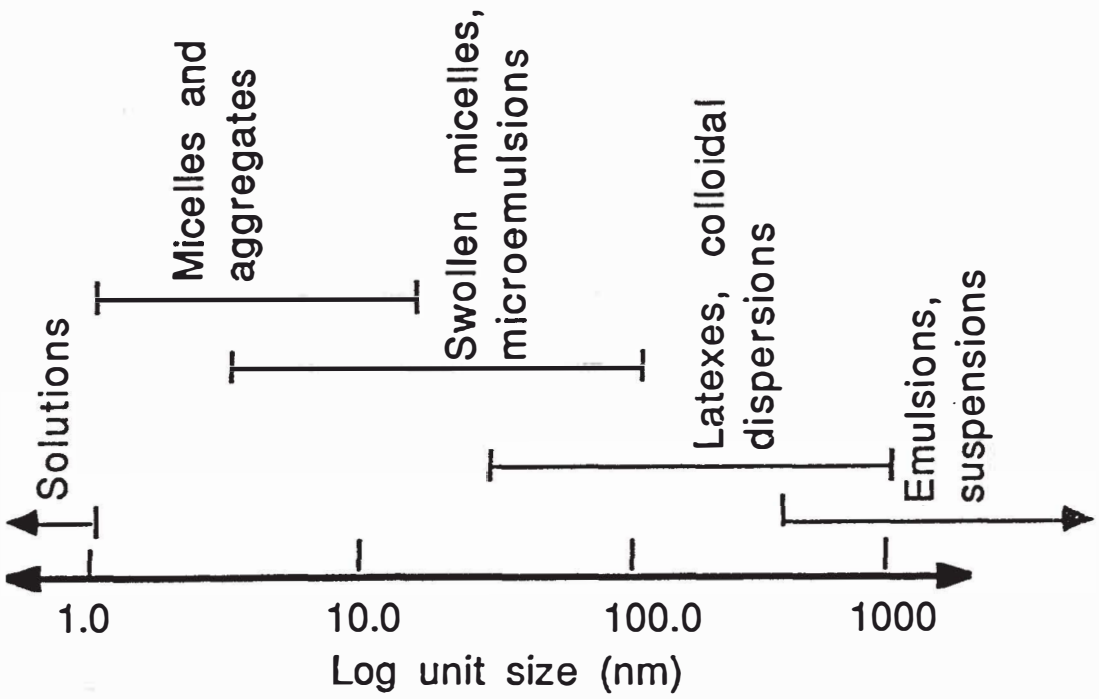

Figure 2 : Approximate size ranges for surfactant assemblies and related structures.

energies of those surfaces or interfaces (Arthur, 1990). It also can be defined as a group of chemical compounds, which usually constitute a hydrocarbon portion and a polar or ionic portion (Benson, 1967; Lucassen, 1981) as illustrated in Figure 3. The term interface denotes a boundary between any two insoluble (or immiscible) phases, the term surface indicates an interface where one phase is a gas, usually air.

In terms of classification, surface active agents are categorised into four types, depending on the nature of the head group. They are cationic, anionic, nonionic and zwittetionic, as shown in Figure 4. Due to their amphiphatic structure, surfactants absorb strongly onto the surface or the interface of air/water or oil/water systems thus altering the properties of these surface or interface. The hydrocarbon portion (tail) or lyophobic group, which can be linear or branched interacts very weakly with the solvent (aqueous solution) molecules in the aqueous environment. The strong interactions of the head group with the solvent is called the lyophilic group. When a surface active agent is dissolved in a solvent, the presence of the lyophobic group in the interior of the solvent will cause a distortion of the solvent liquid structure (the molecules at a surface have higher potential energies than those in the interior). This is because of the stronger interaction with the molecules in the interior of the substance than the widely spaced gas molecules above it, increasing the free energy of the system.